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Mr. Eugene W. Hilgard

Compliments of
Verplanck Colvin.

ON

CERTAIN NEW PHENOMENA

IN

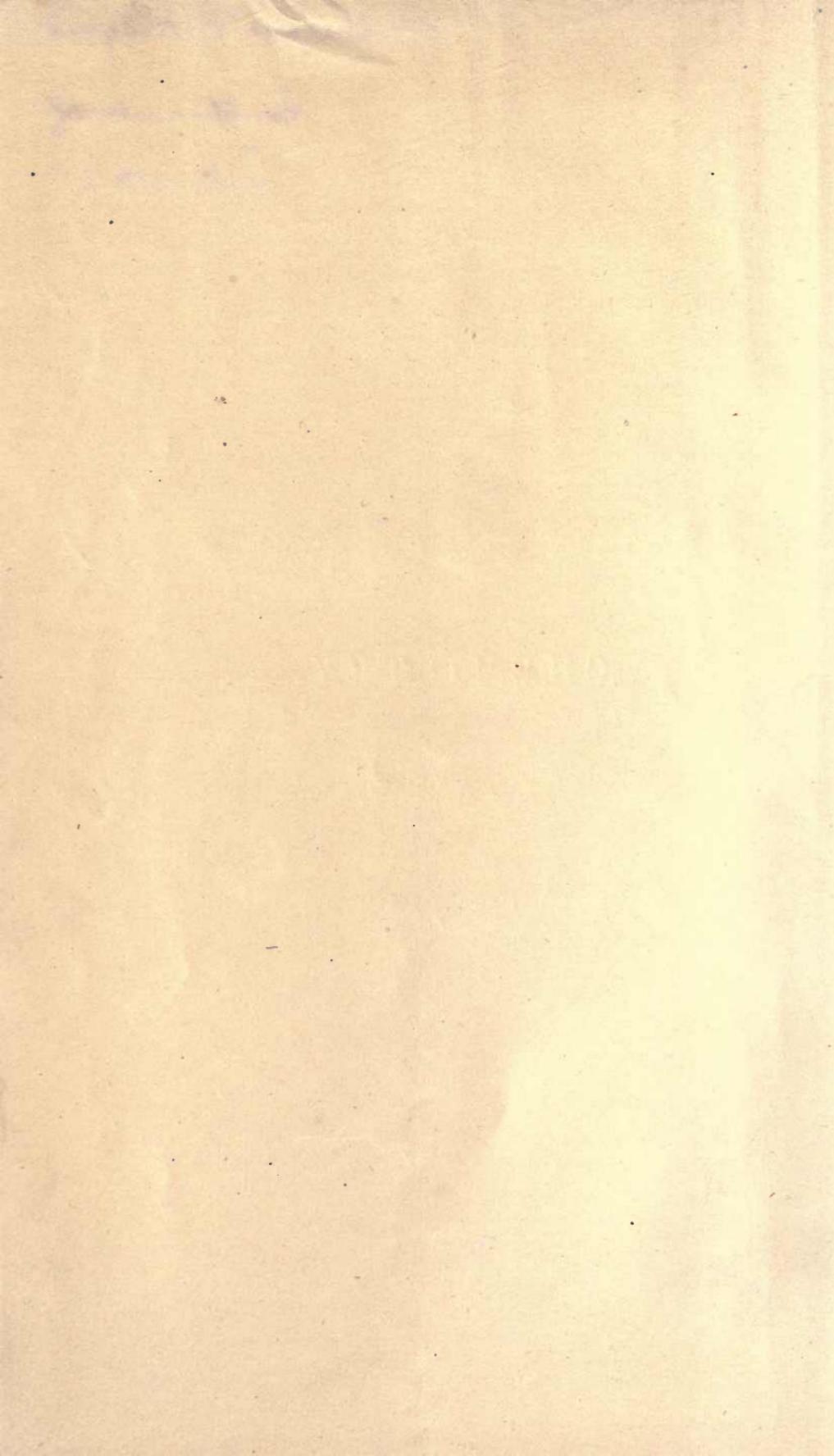
CHEMISTRY,

READ BEFORE

THE ALBANY INSTITUTE, JAN. 2, 1872,

BY

VERPLANCK COLVIN.



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New Phenomena in Chemistry.

The subject of this paper is so broad and varied, the phenomena so interwoven and connected with different branches of material science, that the title is but a slight index to its character, and the paper itself can be only a brief statement of facts, with such deductions as may seem to follow. It might have been entitled "An Account of Mercury and its Amalgams." As that, however, is not exactly the scope of the paper, nor the final object of it, but only the means or vehicle of communicating some ideas—which I hope will prove to be new—it may be allowed to stand here as a suggestion as to the character of the matter which is to follow.

With the discovery, by Humphry Davy, of the metals of the alkalies and earths, a new era opened in Chemistry. The sombre clouds which non-experimenting theorists had cast around the science were suddenly and violently dissipated in the blaze of simple truth, and one of those epochs occurred which must from time to time recur, as man acquires mastery over matter. As the theories of Stahl and his *phlogiston*, had been pressed down and swept away by the discoveries of the previous century, so the accumulated errors of the intervening age were overthrown by Davy's investigations, and the new metals were evolved by electrolysis in the form of amalgams or compounds with mercury. A few of the metals of the earths, however, could not be thus procured, and their existence was only rendered probable by the analogous action of

their salts or oxides when under similar treatment. These discoveries not only gave to Chemistry a list of new metals, but with every one actually evolved, a new amalgam. Thus, to the list of amalgams known to the ancients, were added numerous new compounds, while the general character of the elements so associated was of the most dissimilar kind. One property only seems peculiar to the majority of them, softness or malleability, and ductility. To this class of easily amalgamated elements belong such old metals as gold, silver, copper, tin and lead; and such new metals as potassium, sodium, and calcium.

The other class of metals is peculiar in combining but slightly or not at all with *pure* mercury; and these metals, like those in the preceding class, seem to have but one general characteristic, the reverse of that of the first class, hardness, and at times, even brittleness.

Iron, probably, alone of all the metals known to the ancients, belongs to this second class; while of the new metals which seem to belong to it, chromium, columbium, titanium, manganese, zirconium, and perhaps rhodium are examples. Singularly enough platinum and aluminum, malleable and ductile metals, appear to be attached to this class by reason of the difficulty experienced in directly combining them with pure mercury. It is therefore plain that the proper classification of metals as regards their affinity for mercury, is their separation into these two divisions; the *first* consisting of metals that readily combine with pure mercury; the *second* consisting of metals which refuse to combine with pure mercury, at a moderate temperature.

One of the consequences of the discoveries of Humphry Davy, was the application of the amalgams of potassium and sodium to purposes of exploration in Chemistry. Berzelius and Pontin obtained their ammonium amalgam by the direct electrolysis of aqua-ammonia in contact with

mercury. But afterwards it was observed that this amalgam could be made by the action of potassium or sodium amalgam upon chloride of ammonium. It has been stated that the amalgams thus procured are not exactly similar, the amalgam prepared by the method of Berzelius having a composition according to H. Davy of one part of ammonium to 753 of mercury, and crystallizing in cubes when cooled to zero centigrade; while that prepared with the aid of potassium and sodium amalgam contains according to Gay Lussac and Thénard, one part of ammonium to 1800 parts of mercury.

The discovery by Graham of the metallic nature of hydrogen gas, as evinced by its occlusion in, or alloys with palladium and platinum, enables us to avoid the difficulty of believing in the existence of a metal or "element compounded of gases"—which is an hibernicism—by supposing ammonia to be an alkaline, nitrogen salt of the metal hydrogenium. Then, allowing that the light, cellular or frothy state of the so called ammonium amalgam is owing to the existence throughout the mass of molecules of released nitrogen, clinging to, and recombining with the rapidly re-oxidizing hydrogenium, we account for the ammonical gas afterward given off. We might then suppose that hydrogenium is the metal of the volatile alkali, ammonia, having little resemblance to magnesium, which Graham believed to most resemble it. This, however, is only an hypothesis, and is indeed a digression.

The potassium and sodium amalgams enable us to form, besides this hypothetical amalgam, compounds of mercury with those metals which I have arranged in a second class, as refusing to combine with pure mercury at a moderate or low temperature. The process is simply placing potassium amalgam, or its substitute, excited with some corrosive gas, solution of a salt, aqua-ammonia, water or acid (as the case may require) in contact with the metals to be amal-

gamated. A triple amalgam of mercury, potassium or sodium and "ammonium" (hydrogenium?) is sometimes useful; and I have found zinc amalgam, excited with chlorhydric acid, a powerful agent in producing these results.

And now, before proceeding to describe those phenomena of the discovery of which I can find no record, it is advisable to examine into the nature of mercury and its amalgams, and the present state of our knowledge of its compounds.

Remembering that the fluid mercury with which we are familiar is but the molten substance of a solid, ductile and malleable metal; we arrive at the conclusion that amalgams are simply the *alloys* of mercury, as metals dissolved in melted lead would be alloys of lead. Now the alloys of mercury are peculiarly easy to examine; for even when in the fluid state they do not burn one's fingers, and by analyzing amalgams we are able to discover the condition of the metals contained in them. Having prepared an amalgam of gold and dissolved it in an excess of mercury, I treated the fluid amalgam with nitric acid. When the quicksilver had entirely dissolved, there remained a small spheroid of gold, dark upon the surface, and when broken apart under the hammer, exhibiting a radiating crystallization like that of globular iron pyrites. This, and other experiments (which I have not time to describe), appear to prove that a metal when amalgamated is really dissolved; and it is possible that if the reduction of the amalgam had been less rapid, a well formed crystal of gold might have been obtained. The metals of the second class seem also to be actually dissolved in the mercury.

Our knowledge of the compounds of mercury, as derived from the latest standard works on Chemistry is, singularly imperfect. St. Clair Deville, the famed chemist of the late French empire, the discoverer of the economic process of aluminum manufacture, asserts that metallic

aluminum is not susceptible of amalgamation. Prof. W. A. Miller, in his Inorganic Chemistry (3d edition, p. 425) also says of aluminum: "It does not combine with mercury." Yet in Watts's Dictionary of Chemistry, published in London three years previous to this record in Miller, we find that, "According to Cailletet (*Comp. rend.*, 44, p. 1250) aluminum (also iron and platinum) may be superficially amalgamated by contact with ammonium or sodium amalgam and water; also when immersed in acidulated water, in contact with metallic mercury, forming the negative pole of a voltaic battery." This, published in London 1865, appears to ante-date the discovery by Prof. Henry Wurtz of New York, of the method of amalgamating aluminum with the aid of sodium amalgam (*Trans. Am. Inst.* 1867, p. 766), by some two years; but both discoveries are obviously genuine. Again, both Miller and Watts seem not to be aware of any method of combining mercury directly with metallic platinum, in the form of foil or wire, and describe an indirect method of obtaining it, by the electrolysis of chloride of platinum. Yet potassium or sodium amalgam will readily effect the combination. A few years since, while experimenting with the amalgams of the alkaline metals, I observed that a common iron nail which happened to fall into the amalgam, became coated with mercury. For a time I believed myself the discoverer of iron-amalgam, but on examination I have found mention of it more than thirty years upon record. Aiken (*London Phil. Mag.* XIII, p. 416), shows that it may be accomplished with the aid of zinc amalgam and a solution of chloride of iron. Watts says (l. c. vol. III, p. 887), "Mercury and iron do not unite readily. A viscid amalgam is however obtained by immersing sodium amalgam, containing one per cent of sodium, in a clear, saturated solution of ferrous sulphate. Joule (*Chem. Gaz.*, 1859, p. 339; *Chem. Soc. J.*, XVI, p. 378), has obtained amalgam of iron

by electrolysis of a solution of ferrous sulphate, the negative pole being formed of mercury." None of these authors appear to be aware of any method of directly amalgamating iron, yet H. Davy distinctly states, that either potassium or sodium amalgam will effect the union of mercury with iron and platinum.

Mercury has been employed from time immemorial, in separating the precious metals from their earthy associates. Originally the *pure* metal was employed, as indeed it still is to a considerable extent, held in little rifts or gutters in the trough or sluice where they washed the auriferous sands or pounded ore. This was also the method of amalgamation at the stamp-mills, and it is notorious that much gold passed over the mercury in this process, and escaped. Recently I observed in the gold mining regions of the Rocky mountains, at Central city and Nevada, Colorado, that for the rifts and gutters filled with mercury, they had substituted sheets of copper, superficially amalgamated, over which the ore reduced to a thin mud, or muddy water, was washed, its gold parting and adhering to the surface of the amalgamated copper, and doing so more readily than it would to the surface of pure mercury.

Here we have another instance of that *combination-action*, which we have already noticed in the potassium and sodium amalgams, as evinced by their power to unite mercury with the metals of the second class. It appears that those metals of the first class which are softest, lightest and most easily oxidized (as potassium, sodium, zinc etc.), have the power to enable the harder, heavier and least oxidizable metals of the same class (as copper, silver and gold), to combine more readily with mercury than they would unassisted; and, further, to enable mercury to combine with the metals of the second class, which though generally

harder and more brittle than any of the preceding are often readily oxidized. This *combination-action* separates the alloys of mercury from all other alloys, so far as we now understand them; for, as I have already shown, instead of the mercury always losing power as a metal solvent in proportion as it becomes alloyed—it shows a preference,—and when combined with portions of the readily oxidizable metals, becomes more active and indeed almost ferocious in its appetite for the metals and alloys that are of a highly electro-negative character; while if alloyed with sufficient gold or silver in the first instance, it appears satisfied, phlegmatic and indifferent to further metallic food. Experiments which I have made demonstrate that cyanide of potassium *does not* answer as well as the amalgams of the alkaline metals, in effecting the union of mercury with electro-negative metals, as some have asserted. Its solution is indeed not more effective than aqua-ammonia in producing such results, and what efficacy either of these solutions possess, may be attributed to their cleansing the surface of the metal to be amalgamated.

It now becomes evident that the separation of metals into the two classes is incorrect, as we have here, as in every other general classification in science, no absolute division, but merely extremes and means; the true mean being difficult to determine. The reactions of these amalgams of the electro-positive metals with those metals which are relatively electro-negative, are very instructive. They tend to prove that all the amalgams subsequently formed are the results of *electrical action*, to induce which we have only to place a particle of iron in contact with potassium amalgam and with water. In an instant we have a voltaic battery in active operation; the amalgamated potassium forming the “zincode,” while the iron is the electro-negative element of the battery. Of the metals

present the mercury is the electro-mean, and with the oxidation of the potassium, it passes over to, and effects a combination with the iron.

Thus we arrive at a more correct classification, and at a law of preference of metals and alloys for mercury:

1st Law. Metals that are easily alloyed with mercury give place to, and assist the less amalgamatable metals in combining with mercury, when in the presence of an acid or corrosive liquid or atmosphere, which attacks the metal already amalgamated, and which does not attack, or does not so violently attack the metal to be amalgamated.

2d Law. The more intense the action of the acid or corrosive liquid or gas upon the metal in the original amalgam, the more rapid the formation of the secondary amalgam.

3d Law. The amalgams of electro-positive metals, assist those metals which are relatively electro-negative in combining with mercury.

These laws are the results of certain experiments which, as examples, I will now proceed to describe and illustrate. Placing before us mercury 1st, in the pure state; 2d amalgamated with copper; 3d zinc amalgam; 4th aluminum amalgam; 5th sodium amalgam; 6th potassium amalgam and 7th "ammonium amalgam" (hydrogenium?) we may suppose that we have the extremes and some of the means of mercurial power; mercury in the *pure passive*, and in the compound induced *active* state. To prove that it has a passive and an active condition, it is only necessary to exhibit gold leaf before the pure mercury, and each of the several compounds mentioned.

First. It will be seen that with mercury alone it does not readily amalgamate, and there is no attraction of the gold leaf toward the metal.

Second. Held above the amalgamated copper there is no attraction, but the moment the gold is allowed to touch the surface, it is eagerly seized and devoured.

Third. Held above zinc amalgam excited with chlorhydric acid, the gold leaf begins to waver and tremble slightly as though influenced by the amalgam. Touched to the amalgam it is seized and vanishes instantly.

Fourth. Above the sodium amalgam, excited with water or aqua-ammonia, we have the same symptoms, but even more excitement and eagerness on the part of the gold leaf to pass to the amalgam as it is approached; and the gold is scarcely touched ere it is gone, licked up by the hungry amalgam.

[This action is only seen when but short distances intervene between the gold leaf and amalgam, an eighth or sixteenth of an inch. To perform the experiment successfully, the water should just cover the amalgam, and the edge of the gold leaf should be allowed to dip a little into the water.]

Fifth. With potassium amalgam the action is greater.

Sixth. With the hypothetical hydrogenium or ammonium amalgam, I have found *less action* than the supposedly high electro-positive character of the metal (?) would indicate. This might be accounted for by the porous condition of the amalgam, owing to the gas contained (nitrogen ?) and consequently much diffused state of the "metal." I notice this last experiment and reaction, merely because it may be valuable in determining whether such gaseous metals exist.

The result here seems to be that we have now for the first time, a metallic compound capable of attracting the precious metal gold, when but a short distance intervenes. We can amuse ourselves with the idea that upon this principle a compass may be constructed (a tube charged with the amalgam), which will be to the prospector and

gold hunter as the magnetic dip needle is to the searcher after iron ore. Still, there is something inexplicable about it, for this apparent attraction of gold can hardly be magnetic, and it seems to me we must look for explanation to cohesive, molecular power.

I have shown that the combination of mercury and iron was long since effected; I have now to claim as a discovery the direct amalgamation of *steel*, even when of the toughest and hardest character. The blade of the best pen knife is readily amalgamated, and suffers from the contact, while a plate of fine sheet steel, used in the manufacture of superior instruments, is easily coated with mercury and made to resemble a sheet of silver. By magnetizing soft steel, reducing a sufficient amount of it to filings, and dissolving the filings in mercury, I have procured a magnetic amalgam, in the presence of which an astatic needle is decidedly bewildered. The horseshoe magnet which has this evening been exhibited brightly coated with and upholding an inverted arch of fluid, dripping mercury, lifts quicksilver, it is true, but quicksilver loaded with an amalgam of magnetized steel; an attraction much stronger than that evinced for iron amalgam.

A glass tube properly charged with the magnetic amalgam exhibits the polarity of the compass needle, and has its extremities attracted and repelled by the poles of the magnet in the same manner that the poles of the compass needle are attracted and repelled. This property of the magnetic amalgam is interesting, as it proves that however minutely divided, the atoms of steel still retain their magnetism, and are still influenced by the directive currents of the earth. I have not yet been able to make a very powerful needle of this kind; but, though my observations are very imperfect, am able to say that it seems to point a little more truly to the magnetic north, and from its greater inertia to be less subject to irregular changes

of variation than the ordinary compass needle. The inertia is to be attributed to the assumption by the magnetized steel of a certain portion of the weight or specific gravity of the mercury. When this amalgam is exposed to the oxidizing influence of the atmosphere, it is gradually decomposed, carbon being liberated, and the permanent magnetism vanishing, while iron amalgam remains. This will also finally decompose, pure mercury and ferrous oxide resulting.

Another discovery that I may claim, is the direct amalgamation of *cast-iron*, even of the most brittle and highly carburetted character. This was first effected by means of a compound amalgam of potassium, sodium and "ammonium" with water; but I have since found that a simple amalgam of potassium or sodium is generally sufficient to effect the result. The surface of cast-iron may be amalgamated by placing an electro-positive or active amalgam upon it with water or an acid; a true amalgam may be similarly formed with filings.

In the course of the experiments which led to this discovery, it was my fortune to observe phenomena of an extraordinary character. The usual brilliant surface of mercury is produced when cast-iron is treated with the electro-positive amalgam, and the iron is rapidly "cut" or dissolved. The impurities of the iron, with considerable carbon are released and form a black mud around the button of amalgam. If at this moment, before all the positive metal has been oxidized, the amalgam be removed, washed and allowed to stand, particles of amorphous carbon will be seen to emerge and float upon its mirror-like surface. Whence comes this carbon; why was it not given up before? Has it been amalgamated; and if so, has it not a metallic character? It has been suggested to me that particles of undissolved iron, containing carbon, have been carried bodily into the amalgam, and afterwards dis-

solved, releasing their carbon. However, this is but a conjecture ; the reaction certainly deserves study.

The mere intimation that carbon, the great protean thing in nature, may after all have a metallic origin, is very interesting. Those who believe in the ammonium of Berzelius or the hydrogenium of Graham, need not fear to examine the claims of carbon to a metallic parentage, nor does the existence of such a metal seem so improbable when we remember the electric conductibility of two of the allotropic forms of carbon, gas-coke and plumbago ; the first already replacing, in the voltaic batteries of the present day, the electro-negative elements, platinum, copper etc., while the latter replaces similar electro-negative elements when brushed, in the form of plumbago powder, upon the surface of the mould or plaster-cast which the electro-plater desires to coat with copper or other metal.

If metallic carbonium exists, it may be assumed to be an electro-negative metal. It is true that some forms of carbon are highly inflammable, but are they more so than Graham's hydrogenium ? Graphite at ordinary temperatures is far from combustible, and when it burns, or when the diamond burns in oxygen gas, wrought iron will burn also. No one doubts that iron is a metal, yet one of its purest forms is pyrophoric, taking fire and burning on contact with the atmosphere. To associate graphite with sulphur and phosphorus is to place it, a good conductor of electricity, side by side with the very enemies of traveling magnetism. For how many ages was molybdenite undistinguished from graphite, and who is there now that can instantly distinguish the one from the other ? It is true that molybdenite is a sulphide of molybdenum and graphite a pure allotropic form of carbon, but may there not be one more form of carbon ? There is no substance in nature more readily recognized as a metal by the unlearned than graphite ; to this day it is impossible to

take from it the improper title of black-lead. The experiments of Sir Benjamin Brodie with graphite, his discovery of graphic acid and its combination with ammonia (*graphate of ammonia?*) afford another analogy; for molybdenum has its molybdic acid, and what chemist is there that is not familiar with *molybdate of ammonia*. I have found that contact of native graphite with an electro-positive amalgam and water or acid, produces the same reaction and effervescence, as when a negative metal occupied the place, but an amalgam did not seem to form.

It would appear that the division of elements into metals and non-metals, is as arbitrary as any other absolute division or classification in science; for though the extremes may readily be distinguished,—as gold from fluorine,—the means often approach each other in appearance and in properties.

Besides forming amalgams of steel and cast-iron, I have succeeded in combining mercury directly with crystalline octahedral iron ore (*magnetile*), and with other ores and some furnace products. The loadstone exhibited, coated with mercury, is from the Adirondack mountains. Red fossiliferous hematite ore from Georgia is also readily amalgamated. Bog-iron has so far resisted mercury, save one specimen from the state of Florida, which appeared to receive it slightly. The *slag*, etc., of the Colorado gold-smelting furnaces may also, by means of the compound amalgam, be coated with mercury. Magnesium may be amalgamated with the aid of zinc-amalgam and chlorhydric acid; much heat is evolved, sufficient indeed to burn the hand if laid upon it. Bi-sulphide of carbon, treated with the compound amalgam, is decomposed; sulphides of the alkaline metals result, while another portion of sulphur combines with the mercury, forming true vermillion. Carbon separates in form resembling graphite.

The practical applications of these discoveries are numerous. As mercury dissolves iron and its ores, and finally separates the metal from its impurities of silicon, sulphur and phosphorus, it may prove possible to prepare an iron, nearly as pure as that reduced by hydrogen, for medicinal purposes, by distilling the mercury from the amalgam. In accordance with the laws announced, it is evident that plates of amalgamated zinc or iron are superior to plates of copper in effecting the amalgamation of gold, especially if they be treated with proper acid solutions while the stamped ore is being run out over them. Potassium and sodium amalgams are undoubtedly more effective, but can hardly compete with amalgamated zinc-plates in cheapness.

A great philosopher has said that the results of all experiments should be recorded, nothing being worthless that adds to man's knowledge of the properties of matter. It is my hope that the experiments described, and suggestions here thrown out, may not be altogether valueless.



